

FORM PTO-1390 (REV. 9-2001)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 511.41485X00 filed March 15, 2002	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (If known, see 37 CFR 1.5)	
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INTERNATIONAL APPLICATION NO PCT/JP00/06304		INTERNATIONAL FILING DATE September 14, 2000		PRIORITY DATE CLAIMED September 16, 1999	
TITLE OF INVENTION COMPOSITION, METHODS FOR FORMING LOW-PERMITTIVITY FILM USING THE COMPOSITION, LOW-PERMITTIVITY FILM, AND ELECTRONIC PART HAVING THE LOW-PERMITTIVITY FILM					
APPLICANT(S) FOR DO/EO/US NARITA, TAKENORI MORISIMA, HIROYUKI NOBE, SHIGERU ENOMOTO, KAZUHIRO SAKURAI, HARUAKI TERADA, NOBUKU					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. 4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) a. <input type="checkbox"/> is transmitted hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office(RO/US) 6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 					
Items 11 to 20 below concern document(s) or information included:					
11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 15. <input type="checkbox"/> A substitute specification. 16. <input checked="" type="checkbox"/> A change of power of attorney and/or address letter. 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. 18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 20. <input checked="" type="checkbox"/> Other items or information: Credit Card Payment Form, International Preliminary Examination Report, PCT Request Form, International Search Report w/cited references, International Publication Number WO 01/19922-coversheet					

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JC13 Rec'd PCT/PTO 15 MAR 2002

511.41485X00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: T. NARITA, et al.

Serial No: To be assigned

Filed: March 15, 2002

Title: COMPOSITION, METHODS FOR FORMING LOW-PERMITTIVITY FILM USING THE COMPOSITION, LOW-PERMITTIVITY FILM, AND ELECTRONIC PART HAVING THE LOW-PERMITTIVITY FILM

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington DC 20231

March 15, 2002

Sir:

Please amend the above-identified application, prior to calculation of the filing fee, as follows:

IN THE CLAIMS

Please amend the claims original in the application as follows:

15. (Amended) A method for forming a low-permittivity film which comprises applying the composition according to Claim 1 to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, and then heating the resulting film to condense the siloxane oligomer and remove the thermally decomposable polymer.

16. (Amended) A method for forming a low-permittivity film which comprises applying the composition according to Claim 1 to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, subsequently conducting a first heating

step in which the siloxane oligomer is crosslinked while keeping the thermally decomposable polymer remaining in the film, and then conducting a second heating step in which the thermally decomposable polymer is removed.

Please add the following new claims to the application:

--24. A method for forming a low-permittivity film which comprises applying the composition according to Claim 12 to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, and then heating the resulting film to condense the siloxane oligomer and remove the thermally decomposable polymer.

25. A low-permittivity film formed by the method according to Claim 24.

26. A method for forming a low-permittivity film which comprises applying the composition according to Claim 10 to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, and then heating the resulting film to condense the siloxane oligomer and remove the thermally decomposable polymer.

27. A low-permittivity film formed by the method according to Claim 26.

28. A method for forming a low-permittivity film which comprises applying the composition according to Claim 8 to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly

compatibilized therewith, and then heating the resulting film to condense the siloxane oligomer and remove the thermally decomposable polymer.

29. A low-permittivity film formed by the method according to Claim 28.

30. A method for forming a low-permittivity film which comprises applying the composition according to Claim 5 to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, and then heating the resulting film to condense the siloxane oligomer and remove the thermally decomposable polymer.

31. A low-permittivity film formed by the method according to Claim 30.

32. A method for forming a low-permittivity film which comprises applying the composition according to Claim 12 to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, subsequently conducting a first heating step in which the siloxane oligomer is crosslinked while keeping the thermally decomposable polymer remaining in the film, and then conducting a second heating step in which the thermally decomposable polymer is removed.

33. The method according to Claim 32, wherein said first heating step is conducted at a temperature of 80 to 350°C, and wherein said second heating step is conducted at a temperature of 350 to 500°C.

34. A low-permittivity film formed by the method according to Claim 32.

35. A method for forming a low-permittivity film which comprises applying the composition according to Claim 10 to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, subsequently conducting a first heating step in which the siloxane oligomer is crosslinked while keeping the thermally decomposable polymer remaining in the film, and then conducting a second heating step in which the thermally decomposable polymer is removed.

36. The method according to Claim 35, wherein said first heating step is conducted at a temperature of 80 to 350°C, and wherein said second heating step is conducted at a temperature of 350 to 500°C.

37. A low-permittivity film formed by the method according to Claim 35.

38. A method for forming a low-permittivity film which comprises applying the composition according to Claim 8 to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, subsequently conducting a first heating step in which the siloxane oligomer is crosslinked while keeping the thermally decomposable polymer remaining in the film, and then conducting a second heating step in which the thermally decomposable polymer is removed.

40. A low-permittivity film formed by the method according to Claim 38.

41. A method for forming a low-permittivity film which comprises applying the composition according to Claim 5 to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, subsequently conducting a first heating step in which the siloxane oligomer is crosslinked while keeping the thermally decomposable polymer remaining in the film, and then conducting a second heating step in which the thermally decomposable polymer is removed.

42. The method according to Claim 41, wherein said first heating step is conducted at a temperature of 80 to 350°C, and wherein said second heating step is conducted at a temperature of 350 to 500°C.

43. A low-permittivity film formed by the method according to Claim 41.

44. A low-permittivity film formed by the method according to Claim 39.

45. An electronic part having the low-permittivity film according to Claim 31.

46. An electronic part having the low-permittivity film according to Claim 29.

47. An electronic part having the low-permittivity film according to Claim 27.

48. An electronic part having the low-permittivity film according to Claim 25.

49. An electronic part having the low-permittivity film according to Claim 43.

50. An electronic part having the low-permittivity film according to Claim 40.

51. An electronic part having the low-permittivity film according to Claim 37.

52. An electronic part having the low-permittivity film according to Claim 34.

53. An electronic part having the low-permittivity film according to Claim 44.--

REMARKS

Applicants have amended the claims of the above-identified application, prior to calculation of the filing fee, to delete multiple dependency in the claims. Specifically, each of claims 15 and 16 has been amended to be dependent on claim 1, rather than on any one of claims 1-14.

Moreover, in light of the canceling of multiple dependency, Applicants are adding new claims 24-53 to the application. These new claims 24-53 variously recite subject matter expressly set forth in claims 15-23, and are singly dependent claims within the scope of the multiple dependent claims as originally filed.

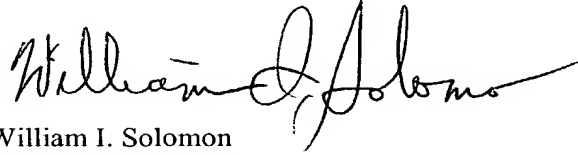
Entry of the present amendments, prior to calculation of the filing fee, and examination of the above-identified application in due course, are respectfully requested.

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned **“Version with markings to show changes made.”**

To the extent necessary, Applicant(s) petitions for an extension of time under 37 CFR §1.136. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to the Deposit Account of Antonelli,

Terry, Stout & Kraus, LLP Account No. 01-2135 (511.41485X00) and please credit
any overpayment of fees to such deposit account.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "William I. Solomon". The signature is fluid and cursive, with a long horizontal stroke extending to the right.

William I. Solomon
Registration No. 28,565

ANTONELLI, TERRY, STOUT & KRAUS, LLP
Suite 1800
1300 North Seventeenth Street
Arlington, Virginia 22209
Telephone: (703) 312-6600
Facsimile: (703) 312-6666

WIS/kmh

VERSION WITH MARKSING TO SHOW CHANGES MADE

In the claims:

Claim 15 has been amended as follows:

15. (Amended) A method for forming a low-permittivity film which comprises applying the composition according to [any one of Claims] Claim 1 [to 14] to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, and then heating the resulting film to condense the siloxane oligomer and remove the thermally decomposable polymer.

Claim 16 has been amended as follows:

16. (Amended) A method for forming a low-permittivity film which comprises applying the composition according to [any one of Claims] Claim 1 [to 14] to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, subsequently conducting a first heating step in which the siloxane oligomer is crosslinked while keeping the thermally decomposable polymer remaining in the film, and then conducting a second heating step in which the thermally decomposable polymer is removed.

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SPECIFICATION

COMPOSITION, METHODS FOR FORMING LOW-PERMITTIVITY FILM
USING THE COMPOSITION, LOW-PERMITTIVITY FILM, AND
5 ELECTRONIC PART HAVING THE LOW-PERMITTIVITY FILM

Field of the Invention

The present invention relates to a composition, a method for forming a low-permittivity film using the
10 composition, a low-permittivity film, and an electronic part having the low-permittivity film. More particularly, the present invention is concerned with a composition from which a low-permittivity film advantageously used as an interlayer insulating film for semiconductor device is
15 formed, a method for forming a low-permittivity film using the composition, a low-permittivity film obtainable from the forming method, and an electronic part having the low-permittivity film, such as a semiconductor device or a multilayer printed circuit board.

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Background Art

In accordance with the fine patterning of the wiring for LSI having a high integration degree, a problem occurs in that an increase in wiring capacitance causes the
25 signal-propagation delay time to increase.

Conventionally, an SiO_2 film having a specific permittivity of about 4.2 formed by a CVD process has been used as an interlayer insulating film, and, for reducing the wiring capacitance of a device and improving the
30 operation speed of LSI, a development of a film having a lower permittivity is desired.

As low-permittivity films, an SiOF film (CVD process) having a specific permittivity of about 3.5, an organic SOG (spin on glass) having a specific permittivity of 2.5 to
35 3.0, and an organic polymer have currently been put into practical use. On the other hand, as materials having a

Fluororesins have a specific permittivity of about 2 and are therefore expected as a low-permittivity material. However, fluororesins have a Tg of 300°C or less, and hence, it is difficult to apply fluororesins as they are to interlayer insulating films for use in LSI. As a method for solving this problem, it has been proposed to use a composite film comprising a fluororesin and polysiloxane as disclosed in Japanese Provisional Patent Publication No. 143420/1997. According to this method, it is possible to obtain an insulating film having a specific permittivity of 2.5 or less, but a thermal decomposition starting temperature of the fluororesin is 400°C or less, so that there is a problem that there is no wide margin in the processing temperature even if the processing temperature for LSI will be lowered in future.

A porous film has attracted attention as a technique which can achieve a specific permittivity of 2.5 or less. As a method for forming a porous film, Japanese Patent Publication No. 12790/1994 has proposed a method in which an organopolysiloxane coating solution containing an organic polymer, such as polystyrene and polyethylene, is applied and subjected to heat treatment, and Japanese Provisional Patent Publication No. 25359/1998 has proposed a method in which polymer particles are dispersed in a polysiloxane precursor. However, in these methods, for forming a porous film, polymer particles are dispersed in a polysiloxane film, and then the polymer particles are removed from the film by heating. Therefore, it is difficult to control the size of the pores in the resulting porous film to 0.1 μm or less. It is expected that the wiring width in the future shrunk LSI is about 0.1 to 0.5

For solving the above problem, Japanese Provisional Patent Publications Nos. 158012/1998 and 217458/1999 have proposed a method in which a porous film is formed from a composition in which both the organic polymer and the polysiloxane are dissolved in a solvent. However, in the method described in Japanese Provisional Patent Publication No. 158012/1998, there is needed a step for gelation using a basic catalyst at a low temperature after a solution of the organic polymer and polysiloxane is applied to a substrate. Therefore, the method poses problems in that the number of steps increases and controlling of the film quality is difficult. Further, in the method described in Japanese Provisional Patent Publication No. 217458/1999, as the organic polymer, a fluoro-resin having high heat resistance is used. Therefore, for completely decomposing the organic polymer, a heat treatment at a high temperature (about 450°C) for a long time is required.

When using an Al wiring which has conventionally been used as a wiring material, the treatment temperature of 450°C is permissible, but a heat treatment for a long time lowers the productivity. Recently, Cu is being used as a wiring material, but, when using a Cu wiring, the permissible treatment temperature is low (about 400°C) and this method is therefore difficult to apply to.

Thus, a method for forming a low-permittivity film, which has a specific permittivity of 2.5 or less and can be formed at about 400°C and applied to an interlayer insulating film for semiconductor device, such as LSI having finer wiring, and for multilayer printed circuit board, has not yet been found.

In the present invention, there is provided a composition from which a low-permittivity film having a specific permittivity of 2.5 or less can be obtained wherein the film can be formed by heating at about 400°C and applied to

an interlayer insulating film for semiconductor device,
such as LSI having finer wiring, and for multilayer printed
circuit board.

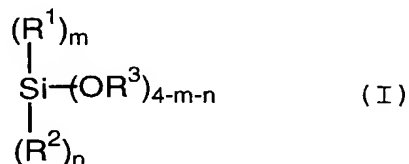
Further, in the present invention, there is provided a low-permittivity film having a specific permittivity of 2.5 or less, which film can be applied to an interlayer insulating film for semiconductor device, such as LSI having finer wiring, and for multilayer printed circuit board.

SUMMARY OF THE INVENTION

The present invention is also directed to a composition comprising (a) a thermally decomposable polymer, (b) a siloxane oligomer, and (c) an organic solvent in which both of components (a) and (b) are soluble.

The present invention is also directed to the above-mentioned composition wherein (b) the siloxane oligomer is a hydrolytic condensation product of an alkoxy silane represented by the following formula (I):

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wherein R^1 and R^2 each represent a non-hydrolyzable group which may be the same or different; R^3 represents an alkyl group having 1 to 6 carbon atoms; and each of m and n is an integer selected from 0 to 3 so that m and n satisfy the relationship: $0 \leq m + n \leq 3$.

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The present invention is also directed to the above-mentioned composition wherein (a) the thermally decomposable polymer is a polymer which exhibits a weight loss at 250°C of less than 5% based on the weight at 150°C, as measured by a thermogravimetric analysis in which the temperature is elevated from 30°C or lower at a temperature elevation rate of 20°C/min under an air stream.

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The present invention is also directed to the above-mentioned composition wherein (a) the thermally decomposable polymer is a polymer which exhibits a weight loss at 400°C of 80% or more based on the weight at 150°C, as measured by a thermogravimetric analysis in which the

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temperature is elevated from 30°C or lower at a temperature elevation rate of 20°C/min under an air stream.

The present invention is also directed to the above-mentioned composition wherein (a) the thermally decomposable polymer is a fluorine-free polymer.

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The present invention is also directed to the above-mentioned composition wherein (a) the thermally decomposable polymer is a methacrylic polymer or an acrylic polymer.

The decomposition temperature of (a) the thermally decomposable polymer can be confirmed by using a thermogravimetric analysis. In the present invention, the decomposition temperature of (a) the thermally decomposable polymer was confirmed by performing a thermogravimetric analysis with the following apparatus and conditions.

10 Temperature elevation starting temperature: 30°C or
lower

Sample weight: 10 mg

As the base weight for (a) the thermally decomposable polymer before starting decomposition, the weight of it at 150°C in the course of the temperature elevation is used. The weight loss at 150°C or lower is considered to be caused by removal of moisture adsorbed, i.e., factors other than the decomposition of (a) the thermally decomposable polymer.

Examples of (a) the thermally decomposable polymers which exhibit a weight loss at 250°C of 5 % or more include polyether polymers such as tetramethylene oxide and polyethylene glycol.

Examples of (a) the thermally decomposable polymers which exhibit a weight loss at 250°C of less than 5% include vinyl ester polymers such as polyvinyl acetate, methacrylate polymers such as polymethyl methacrylate, acrylate polymers such as polymethyl acrylate; polyvinyl alcohol, polyethylene imine and fluororesins.

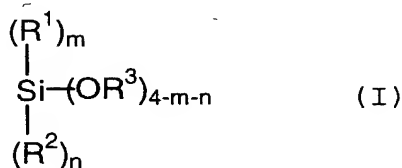
Examples of (a) the thermally decomposable polymers which exhibit a weight loss at 250°C of less than 5 % and exhibit a weight loss at 400°C of 80% or more include methacrylate polymers such as polymethyl methacrylate, acrylate polymers such as polymethyl acrylate; and

polyethylene imine.

Of these, methacrylate polymers and acrylate polymers such as polymethyl methacrylate and polymethyl acrylate exhibit a weight loss at 250°C of less than 2 % and exhibit
5 a weight loss at 400°C of 90 % or more, and are therefore particularly excellent as (a) the thermally decomposable polymer to be used in the composition of the present invention.

A fluororesin has a heat resistance at about 400°C,
10 and, removal of the polymer by heating at about 400°C requires a long time, and thus the fluororesin is disadvantageous from a practical point of view. Therefore, as (a) the thermally decomposable polymer, it is preferred to use a fluorine-free polymer.

15 In the present invention, as (b) the siloxane oligomer, for example, there may be mentioned a hydrolytic condensation product of an alkoxysilane represented by the following formula (I):



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wherein R¹ and R² each represent a non-hydrolyzable group which may be the same or different; R³ represents an alkyl group having 1 to 6 carbon atoms; and each of m and n is an integer selected from 0
25 to 3 so that m and n satisfy the relationship: 0 ≤ m + n ≤ 3.

The hydrolytic condensation product may be either a condensation product partially hydrolyzed or a condensation product completely hydrolyzed.

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As the non-hydrolyzable group, non-hydrolyzable groups having 1 to 4 carbon atoms are preferred from the viewpoint of availability with ease. Examples of non-hydrolyzable groups include organic groups having a reactive group such

The hydrolytic condensation product in the present invention is a hydrolytic condensation product or a mixture of two or more hydrolytic condensation products selected from the group consisting of the hydrolytic condensation product wherein the relationship: $m = n = 0$ is satisfied in the formula (I), the hydrolytic condensation product wherein the relationship: $m + n = 1$ is satisfied, the hydrolytic condensation product wherein the relationship: $m + n = 2$ is satisfied, and the hydrolytic condensation product wherein the relationship: $m + n = 3$ is satisfied.

The alkoxysilane where $m + n$ equals 3 has only one hydrolyzable group in the molecule thereof, as a matter of course, and it cannot solely form a hydrolytic condensation product. Therefore, the $m + n = 3$ alkoxysilane is used in combination with the alkoxysilane where $m = n = 0$, the alkoxysilane where $m + n = 1$, or the alkoxysilane where $m + n = 2$ for suppressing an excess reaction of a hydrolytic condensation product of the alkoxysilane in a solution. It is preferred that the alkoxysilane where $m + n = 3$ is present in an amount of 10 mol% or less based on the total

By adding an appropriate amount of the alkoxysilane where $m = n = 0$ having no non-hydrolyzable group, the resulting low-permittivity film can be improved in

Specific examples of these alkoxysilanes are shown below.

There may be mentioned tetraalkoxysilanes such as tetramethoxysilane, tetraethoxysilane and tetrapropoxysilane, monoalkyltrialkoxysilanes such as methyltrimethoxysilane and methyltriethoxysilane, monoaryltrialkoxysilanes such as phenyltrimethoxysilane and phenyltriethoxysilane, monoalkenyltrialkoxysilanes such as vinyltrimethoxysilane and vinyltriethoxysilane, fluorine-containing alkoxysilanes such as trifluoromethyltrimethoxysilane, trifluoropropyltrimethoxysilane, pentafluorobutyltrimethoxysilane, nonafluorohexyltrimethoxysilane, tridecafluorooctyltrimethoxysilane, heptadecafluorodecyltrimethoxysilane, heptadecafluorodecylmethyldimethoxysilane, heptadecafluoroundecyltrimethoxysilane, (4-perfluorobutylphenyl)trimethoxysilane, (4-perfluorohexylphenyl)trimethoxysilane and (4-perfluorooctylphenyl)trimethoxysilane, epoxysilanes such as γ -glycidoxypropyltrimethoxysilane and γ -glycidoxypropyltriethoxysilane, aliphatic aminosilanes such as γ -aminopropylmethyldiethoxysilane and γ -aminopropyltriethoxysilane, and aromatic ring-containing aminosilanes such as aminophenyl-

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trimethoxysilane, aminophenyltriethoxysilane and N-phenyl-
γ-aminopropyltrimethoxysilane. These alkoxyxilanes are
used individually or in combination.

5 The condensation reaction of the alkoxyxilane can be
conducted by a conventional manner. For example, there can
be mentioned a method in which water is added to the
alkoxyxilane in the presence of a solvent and a catalyst to
effect a hydrolytic condensation reaction.

In this case, if desired, heating may be conducted.
10 As a catalyst, an inorganic acid such as hydrochloric acid,
nitric acid and sulfuric acid, and an organic acid such as
formic acid, oxalic acid and acetic acid can be used. In
general, it is preferred that the hydrolytic condensation
product has a weight average molecular weight (as measured
15 by gel permeation chromatography (GPC) using a calibration
curve obtained by standard polystyrene) in the range of 500
to 10000 from the viewpoint of increasing compatibility of
the hydrolytic condensation product with a thermally
decomposable polymer and for facilitating dissolution of
20 the hydrolytic condensation product in a solvent. Then, if
desired, water present in the system is removed by distil-
lation, and further the catalyst may be removed using an
ion-exchange resin.

With respect to the method for preparing a mixed
25 solution of (a) the thermally decomposable polymer and (b)
the siloxane oligomer, there is no particular limitation as
long as a uniform solution can be finally prepared, and, as
examples of methods, there may be mentioned the following
(1) to (3) methods.

30 (1) A method in which a solution of (a) the thermally
decomposable polymer and a solution of (b) the siloxane
oligomer are separately prepared preliminarily, and then
they are mixed together. In this method, the solution of
(b) the siloxane oligomer may be directly prepared by using
35 a solvent which is compatible with the solution of (a) the
thermally decomposable polymer, or (b) the siloxane

(a) the thermally decomposable polymer may have a functional group, but it is not preferred that a crosslinking reaction of the functional group with the hydrolyzable

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group in (b) the siloxane oligomer and a silanol group formed by the hydrolysis occurs. When crosslinking occurs between (a) the thermally decomposable polymer and (b) the siloxane oligomer, after removing (a) the thermally decomposable polymer by heating, a silanol group is formed to deteriorate the low permittivity and low moisture absorption property of the resulting film.

When a crosslinking reaction does not occur between the functional group of (a) the thermally decomposable polymer and the hydrolyzable group in (b) the siloxane oligomer and the silanol group formed by the hydrolysis but only an interaction occurs therebetween due to polarity of the functional group, the compatibility of (a) the thermally decomposable polymer with (b) the siloxane oligomer is improved, so that a more uniform low-permittivity film can be obtained.

In the present invention, examples of (c) the organic solvents include alcohol solvents such as methanol, ethanol propanol and butanol, fluorine-containing alcohol solvents such as $\text{CF}_3\text{CH}_2\text{OH}$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$ and $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OH}$, acetate solvents such as methyl acetate, ethyl acetate, propyl acetate and butyl acetate, lactone solvents such as γ -lactone, glycol acetate solvents such as ethylene glycol monomethyl acetate and ethylene glycol diacetate, amide solvents such as N-methyl-2-pyrrolidone, and glycol ether solvents. These are used individually or in combination.

Among these (c) organic solvents, it is preferred to use (c)' an organic solvent in which both of (a) the thermally decomposable polymer and (b) the siloxane oligomer are soluble.

The amount of (c) the organic solvent to be used is appropriately selected depending on the desired solution viscosity or thickness of the coating film, but, for example, when a coating film having a thickness of 0.1 to 5 μm is to be obtained by a spin coating method, it is preferred to use the organic solvent in an amount such that the solid

content of the resulting composition becomes 1 to 20% by weight.

The formation of a low-permittivity film using the composition of the present invention can be achieved by, for example, applying the composition to a substrate to form a composite film which comprises (a) the thermally decomposable polymer and (b) the siloxane oligomer evenly compatibilized therewith, and then heating the resulting film to condense (b) the siloxane oligomer and remove (a) the thermally decomposable polymer.

In this method, in the heating step after application, it is important that (b) the siloxane oligomer is condensed in a state such that (a) the thermally decomposable polymer is present in the film to form a network of polysiloxane.

15 When the decomposition of (a) the thermally decomposable polymer starts before forming the network of polysiloxane, the film suffers shrinkage due to the decomposition of thermally decomposable polymer (a), so that the low permittivity of the resulting film may possibly be deteriorated.

For obtaining a low-permittivity film having high heat resistance and low moisture absorption property, it is preferred to use a siloxane oligomer having a non-hydrolyzable group as (b) the siloxane oligomer. When such (b) a siloxane oligomer is heated without using a basic catalyst, condensation starts at 150°C or higher. Then, the condensation proceeds to form a network of polysiloxane, and the formation of the structure of the film is substantially completed at 250°C or higher. Therefore, in the present invention, for obtaining a low-permittivity film having high heat resistance and low moisture absorption property, (a) the thermally decomposable polymer preferably has a decomposition starting temperature of 150°C or higher, more preferably 250°C or higher. From such a point of view, it is preferred that (a) the thermally decomposable polymer is a polymer which exhibits a weight loss at 250°C of less than 5 %, and further which exhibits a weight loss at 400°C

of 80 % or more, each based on the weight at 150°C, as measured by a thermogravimetric analysis in which the temperature is elevated from 30°C or lower at a temperature elevation rate of 20°C/min under an air stream.

5 Further, for obtaining a low-permittivity film by the method of the present invention, it is preferred that (a) the thermally decomposable polymer is satisfactorily removed by heating. When the removal of (a) the thermally decomposable polymer is incomplete, the low permittivity of
10 the resulting film is tend to be impaired.

When the present invention is applied to formation of an interlayer insulating film for LSI, the heating temperature employed varies depending on the type of the wiring material. The heating temperature when using a conventional Al wiring is 400 to 450°C, and it is expected that the
15 heating temperature when using a Cu wiring in future will be expected to be about 380 to 430°C. Therefore, when the present invention is applied to an LSI using a Cu wiring, it is preferred that (a) the thermally decomposable polymer
20 is satisfactorily removed at 400°C or less. Further, also in an LSI using an Al wiring, it is preferred that (a) the thermally decomposable polymer is removed at 400°C or less from the viewpoint of reducing the change in permittivity with the heating temperature.

25 Examples of coating methods for the composition of the present invention include a spin coating method, a dipping method, a potting method, a die coating method and a spray coating method, and the coating method may be appropriately selected depending on the form of the object to be coated
30 and the film thickness needed. When the composition of the present invention is applied to an interlayer insulating film for semiconductor device, a spin coating method is preferred from the viewpoint of obtaining a narrow film thickness distribution. When the composition is applied to
35 an interlayer insulating film for multilayer printed circuit board, a die coating method as well as a spin

25 Preparation example 2
(Siloxane oligomer solution ② obtained by hydrolytic
condensation reaction using tetramethoxysilane in an amount
of 0.4 mol based on 1 mol of monomethyltrimethoxysilane;
solvent: propylene glycol monopropyl ether)

30 Siloxane oligomer solution ② was prepared in substantially the same manner using propylene glycol monopropyl ether as a solvent. With respect to the resulting siloxane oligomer, a molecular weight was measured by GPC. As a result, it was found that the weight average molecular weight in terms of polystyrene was about 1500. After
35 synthesis, the solution was stored in a freezer (at -18°C).

Polymethyl methacrylate (PMMA) having a weight average molecular weight in terms of polystyrene of 120,000 was dissolved in γ -butyrolactone to obtain Solution ③ having a polymer concentration of 10% by weight.

Polyvinyl acetate (PVAc) having a weight average molecular weight in terms of polystyrene of 12,800 was dissolved in propylene glycol monopropyl ether to obtain Solution ④ having a polymer concentration of 10% by weight.

In a flask were mixed 100 g of Siloxane oligomer solution ① and 133 g of Polymer solution ③ together and the mixture was stirred for one hour. Then, the resulting mixture was allowed to stand at room temperature for one day to obtain Solution A. The obtained composition has a nonvolatile content of about 14% by weight, and the weight ratio of the siloxane oligomer to the polymer is 150 parts by weight of the siloxane oligomer based on 100 parts by weight of the polymer.

In a flask were mixed 100 g of Siloxane oligomer solution ① and 50 g of Polymer solution ③ together and the mixture was stirred for one hour. Then, the resulting mixture was allowed to stand at room temperature for one day to obtain Solution B. The obtained composition has a nonvolatile content of about 17% by weight. The weight ratio of the siloxane oligomer to the polymer is 400 parts by weight of the siloxane oligomer based on 100 parts by weight of the polymer.

In a flask were mixed 100 g of Siloxane oligomer solution ② and 133 g of Polymer solution ④ together and the mixture was stirred for one hour. Then, the resulting mixture was allowed to stand at room temperature for one

day to obtain Solution C. The obtained composition has a nonvolatile content of about 14% by weight, and the weight ratio of the siloxane oligomer to the polymer is 150 parts by weight of the siloxane oligomer based on 100 parts by weight of the polymer.

Example 4

In a flask were mixed 100 g of Siloxane oligomer solution ② and 50 g of Polymer solution ④ together and the mixture was stirred for one hour. Then, the resulting mixture was allowed to stand at room temperature for one day to obtain Solution D. The obtained composition has a nonvolatile content of about 17% by weight. The weight ratio of the siloxane oligomer to the polymer is 400 parts by weight of the siloxane oligomer based on 100 parts by weight of the polymer.

Comparative examples 1 and 2, and Examples 5 to 8

Using Siloxane oligomer solution ①, Siloxane oligomer solution ②, Coating solution A, Coating solution B, Coating solution C, and Coating solution D, coating films were formed by a spin coating method. As a substrate, a bare silicon wafer was used. The rotary speed for coating was adjusted per coating solution so that the thickness of the film after final curing (at 400 to 450°C) became about 4500 to 5000 Å. After completion of the spin coating, the resulting film was baked by a hot plate at 150°C/30 sec and at 250°C/30 sec successively. The final curing was conducted by using a vertical furnace in a nitrogen gas atmosphere at 400, 425 and 450°C/1 hr.

With respect to each of the obtained films, a specific permittivity was measured. The specific permittivity was determined by a method in which an Al electrode having a diameter of 2 mm was formed on a film, and a capacitance of the capacitor formed by the Al electrode and the silicon wafer was measured to calculate a specific permittivity from the thickness of the film and the area of the Al electrode. The measurement of capacitance was conducted

using an impedance analyzer at 10 kHz. The thickness of a film was measured by using ellipsometry. The results of the measurement of specific permittivity are shown in Table 1.

5

Table 1

	Used solution	Specific permittivity		
		400°C	425°C	450°C
Comparative example 1	Solution ①	3.1	3.0	2.9
Comparative example 2	Solution ②	3.1	3.0	2.9
Example 5	Solution A	2.2	2.1	2.1
Example 6	Solution B	2.6	2.5	2.5
Example 7	Solution C	2.7	2.5	2.3
Example 8	Solution D	3.0	2.7	2.6

With respect to each of PMMA and PVAc used in Polymer solutions ③ and ④, a thermogravimetric analysis was conducted. The conditions for the measurement are shown below.

Apparatus: TG-DTA6200 (manufactured by Seiko Instruments Inc.)
 Temperature elevation starting temperature: 30°C or lower

Temperature elevation rate: 20°C/min

Sample weight: 10 mg

Atmosphere: Air at 200 ml/min

For avoiding the influence of the weight loss caused by the factors other than the decomposition of the polymer, a weight loss at 250°C and a weight loss at 400°C, each based on the weight of the polymer at 150°C, were calculated from the results of measurement. The results are shown in Table 2.

25

For confirming the influence of moisture absorption on
25 each of the films formed in Examples 5 to 8, a wafer having
formed thereon the film was allowed to stand for one week
in a room controlled at a temperature of 23°C at a humidity
of 40%, and then a specific permittivity was measured
again. As a result, it was found that the increase in
30 permittivity was 0.1 at maximum. This result indicates
that each of the obtained films has a low moisture
absorption property.

With respect to each of the films formed in Examples 5 to 8, a cross-section was observed through an electron microscope at a magnification of 100,000 times. As a result, it was found that definite pores seen in a film called porous film are not observed in each film. There is no means effective for observing micro-pores currently, but it is presumed that, when pores are assumed to be formed in each film, the pores have a size of 0.01 μm or less. Therefore, the obtained films can be applied to shrunk LSI having a wiring width as small as about 0.1 μm .

In Examples 5 to 8, there are shown examples in which the siloxane oligomer solution and the thermally decomposable polymer solution were separately prepared, and then mixed together to prepare a coating solution. When an alkoxysilane was subjected to hydrolytic condensation in a solution having dissolved therein a thermally decomposable polymer to prepare a coating solution, the same results were obtained.

20 Industrial applicability

From the composition of the present invention, a low-permittivity film having a specific permittivity of 2.5 or less can be obtained wherein the film can be formed by heating at about 400°C and applied to an interlayer insulating film for semiconductor device, such as LSI having finer wiring, and for multilayer printed circuit board.

By the method for forming a low-permittivity film of the present invention, a low-permittivity film having a specific permittivity of 2.5 or less can be obtained with ease in high yield wherein the film can be formed by heating at about 400°C and applied to an interlayer insulating film for semiconductor device, such as LSI having finer wiring, and for multilayer printed circuit board.

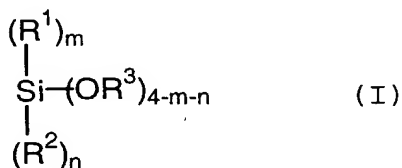
The low-permittivity film of the present invention has

6. The composition according to Claim 5, wherein (a) the thermally decomposable polymer is a fluorine-free polymer.

10 8. A composition comprising

- (a) a thermally decomposable polymer,
- (b) a siloxane oligomer, and
- (c) an organic solvent in which both of said components (a) and (b) are soluble.

10. The composition according to Claim 9, wherein (b) the siloxane oligomer is a hydrolytic condensation product of an alkoxy silane represented by the following formula (I):



11. The composition according to Claim 10, wherein (a) the thermally decomposable polymer is a polymer which exhibits a weight loss at 250°C of less than 5% based on the weight

12. The composition according to Claim 11, wherein (a) the thermally decomposable polymer is a polymer which exhibits a weight loss at 400°C of 80% or more based on the weight at 150°C, as measured by a thermogravimetric analysis in which the temperature is elevated from 30°C or lower at a temperature elevation rate of 20°C/min under an air stream.

15 14. The composition according to Claim 12, wherein (a) the
thermally decomposable polymer is a methacrylate polymer or
an acrylate polymer.

16. A method for forming a low-permittivity film which comprises applying the composition according to any one of Claims 1 to 14 to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, subsequently conducting a first heating step in which the siloxane oligomer is crosslinked while keeping the thermally decomposable polymer remaining in the film, and then conducting a second heating step in which the thermally decomposable polymer is removed.

- 28 -

17. The method according to Claim 16, wherein said first heating step is conducted at a temperature of 80 to 350°C, and wherein said second heating step is conducted at a temperature of 350 to 500°C.

5

18. A low-permittivity film formed by the method according to Claim 15.

19. A low-permittivity film formed by the method according to Claim 16.

10

20. A low-permittivity film formed by the method according to Claim 17.

21. An electronic part having the low-permittivity film according to Claim 18.

15

22. An electronic part having the low-permittivity film according to Claim 19.

20

23. An electronic part having the low-permittivity film according to Claim 20.

Abstract

The present invention provides a composition comprising (a) a thermally decomposable polymer and (b) a siloxane oligomer evenly dissolved in (c) an organic solvent; a composition comprising (a) a thermally decomposable polymer, (b) a siloxane oligomer, and (c) an organic solvent in which both of the ingredients (a) and (b) are soluble; a method for forming a low-permittivity film characterized by applying the composition to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith and then heating the resulting film to condense the siloxane oligomer and remove the thermally decomposable polymer; a method for forming a low-permittivity film characterized by applying the composition to a substrate to form a composite film comprising the thermally decomposable polymer and the siloxane oligomer evenly compatibilized therewith, subsequently conducting a first heating step in which the siloxane oligomer is crosslinked while keeping the thermally decomposable polymer remaining in the film, and then conducting a second heating step in which the thermally decomposable polymer is removed; a low-permittivity film formed by either of the methods for low-permittivity film formation; and an electronic part having the low-permittivity film.

DECLARATION AND POWER OF ATTORNEY FILED WITH U.S. DESIGNATED OFFICE UNDER 35 U.S.C. 371(c)(4)

As a below named inventor, I/we hereby declare that:

My/Our residence, post office address and citizenship are as stated below next to my/our name, I/we believe that I/we are the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

COMPOSITION, METHODS FOR FORMING LOW-PERMITTIVITY FILM USING THE
COMPOSITION, LOW-PERMITTIVITY FILM, AND ELECTRONIC PART HAVING THE
LOW-PERMITTIVITY FILM

the specification of which was filed as PCT International Application No. PCT/JP00/06304

filed September 14, 2000 and was amended on _____
 (if applicable)

I/We hereby state that I/we have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I/We acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I/We hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Priority Claimed

<u>261391/1999</u> (Number)	<u>Japan</u> (Country)	<u>16/September/1999</u> (Day/Month/Year Filed)	<input checked="" type="checkbox"/> Yes	<input type="checkbox"/> No
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	<input type="checkbox"/> Yes	<input type="checkbox"/> No
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	<input type="checkbox"/> Yes	<input type="checkbox"/> No
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	<input type="checkbox"/> Yes	<input type="checkbox"/> No
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	<input type="checkbox"/> Yes	<input type="checkbox"/> No
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	<input type="checkbox"/> Yes	<input type="checkbox"/> No

I/We hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I/we acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

_____ (Application Serial No.)	_____ (Filing Date)	_____ (Status: patented, pending, abandoned)
_____ (Application Serial No.)	_____ (Filing Date)	_____ (Status: patented, pending, abandoned)
_____ (Application Serial No.)	_____ (Filing Date)	_____ (Status: patented, pending, abandoned)
_____ (Application Serial No.)	_____ (Filing Date)	_____ (Status: patented, pending, abandoned)

I hereby appoint as principal attorneys; Donald R. Antonelli, Reg. No. 20,296; David T. Terry, Reg. No. 20,178; Melvin Kraus, Reg. No. 22,466; William I. Solomon, Reg. No. 28,565; Gregory E. Montone, Reg. No. 28,141; Ronald J. Shore, Reg. No. 28,577; Donald E. Stout, Reg. No. 26,422; Alan E. Schiavelli, Reg. No. 32,087; James N. Dresser, Reg. No. 22,973 and Carl I. Brundidge, Reg. No. 29,621 to prosecute and transact all business connected with this application and any related United States application and international applications. Please direct all communications to the following address:

Antonelli, Terry, Stout & Kraus
Suite 1800
1300 North Seventeenth Street
Arlington, Virginia 22209
Telephone: (703) 312-6600
Fax: (703) 312-6666

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United State Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Parent issued thereon.

	(Full Name)	(Signature)
Date <u>March 5, 2002</u>	Inventor <u>Takenori NARITA</u>	<u>Takenori Narita</u>
Residence <u>Hitachi-shi, Ibaraki, Japan</u>		Citizenship <u>Japan JPX</u>
Post Office Address <u>Yamazaki-ryo 129, 2-9, Higashi-cho 4-chome, Hitachi-shi, Ibaraki 317-0061 JAPAN</u>		
Date <u>March 5, 2002</u>	Inventor <u>Hiroyuki MORISIMA</u>	<u>Hiroyuki Morisima</u>
Residence <u>Hitachi-shi, Ibaraki, Japan</u>		Citizenship <u>Japan JPX</u>
Post Office Address <u>19-3, Kamiiai-cho 2-chome, Hitachi-shi, Ibaraki 319-1417 JAPAN</u>		
Date <u>March 5, 2002</u>	Inventor <u>Shigeru NOBE</u>	<u>Shigeru Nobe</u>
Residence <u>Hitachi-shi, Ibaraki, Japan</u>		Citizenship <u>Japan JPX</u>
Post Office Address <u>21-2-402, Nishinarusawa-cho 3-chome, Hitachi-shi, Ibaraki 316-0032 JAPAN</u>		
Date <u>March 5, 2002</u>	Inventor <u>Kazuhiro ENOMOTO</u>	<u>Kazuhiro Enomoto</u>
Residence <u>Hitachi-shi, Ibaraki, Japan</u>		Citizenship <u>Japan JPX</u>
Post Office Address <u>Yamazaki-ryo 131, 2-9, Higashi-cho 4-chome, Hitachi-shi, Ibaraki 317-0061 JAPAN</u>		
Date <u>March 5, 2002</u>	Inventor <u>Haruaki SAKURAI</u>	<u>Haruaki Sakurai</u>
Residence <u>Hitachi-shi, Ibaraki, Japan</u>		Citizenship <u>Japan JPX</u>
Post Office Address <u>Yamazaki-ryo 303, 2-9, Higashi-cho 4-chome, Hitachi-shi, Ibaraki 317-0061 JAPAN</u>		
Date <u>March 5, 2002</u>	Inventor <u>Nobuko TERADA</u>	<u>Nobuko Terada</u>
Residence <u>Hitachi-shi, Ibaraki, Japan</u>		Citizenship <u>Japan JPX</u>
Post Office Address <u>3-16, Suehiro-cho 2-chome, Hitachi-shi, Ibaraki 316-0006 JAPAN</u>		
Date _____	Inventor _____	
Residence _____		Citizenship _____
Post Office Address _____		
Date _____	Inventor _____	
Residence _____		Citizenship _____
Post Office Address _____		
Date _____	Inventor _____	
Residence _____		Citizenship _____
Post Office Address _____		
Date _____	Inventor _____	
Residence _____		Citizenship _____
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